RAW MATERIALS

UDC 666.189.3:666.122.2

PROSPECTS FOR USE OF FINELY DISPERSE QUARTZ SANDS IN PRODUCTION OF FOAM-GLASS CRYSTALLINE MATERIALS

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Translated from *Steklo i Keramika*, No. 9, pp. 28 – 30, September, 2008.

Use of finely disperse Tuganskoe quartz sands (Tomsk Oblast) in production of foam-glass crystalline materials by low-temperature synthesis of glass granulate instead of cullet was investigated. The important possibility of manufacturing foam-glass crystalline materials with basic process properties as good as traditional foam glass made from cullet was established.

Foam glass has many unique properties, but its high cost on one hand, and the almost total absence of manufacturers in the Russian market on the other have impeded wide use of this material. One problem for domestic enterprises, both manufacturers, and those wishing to set up foam glass production, is the lack of a sufficient amount of secondary cullet, used in traditional foam-glass production technology, for organizing profitable production. In particular, manufacture of foam glass at Tomsk House Building Co. is directly dependent on the amount of cullet formed at Tomsk Electric Lamp Factory and is limited to 7000 m^3/year, which only partially satisfies the company's needs.

The existence of large resources of natural raw material creates the grounds for expanding the mineral-raw material base for production of foam glass. It is necessary to consider that glass melting from raw materials implies important investments in organizing technologically complex, specialized, and frequently power-intensive production. This problem can be solved by using local natural raw material or industrial wastes from other plants by low-temperature synthesis of material to replace cullet, conditionally called glass granulate, which would allow increasing the competitiveness of foam glass in comparison to other heat-insulating materials.

We investigated the possibility of synthesizing glass granulate from the finely disperse fraction of quartz sands for different applications at temperatures of 800 – 950°C and making foam glass from it.

The Tuganskoe sand fraction investigated (100 μm maximum particle size) is the product of concentration of quartz sand after separation of zirconium-ilmenite ore and kaolin. The deposit is located 30 km from Tomsk and the ore sand reserves are approximately 124.7 million m^3, i.e., sufficient for use of the quartz constituent of the deposit in foam glass production.

The 98% concentrated sand consists of quartz minerals with impurities in the form of feldspar and mica, confirmed by x-ray phase analysis.

The chemical composition of concentrated finely disperse Tuganskoe sand (%[2]) is: 98.15 SiO_2, 0.67 Al_2O_3, 0.05 Fe_2O_3, 0.07 CaO, 0.02 MgO, 0.06 TiO_2, and 0.90 calcination loss. Note the relatively high silica content and the relative low iron oxide content.

The electron microscopic studies showed that Tuganskoe sand is basically represented by grains with an acute-angle, fragmented shape, a rough surface with defects in the form of microcracks and pits (Fig. 1), which serves as grounds for increasing the chemical activity of the batch based on it.

The fine dispersion of the initial components of the batch has the basic effect for conducting reactions of silicate and glass formation in the low-temperature region. The higher the specific surface area and correspondingly the greater the contact area of the contacting components, the more active the physicochemical processes in the batch during heat treatment. One important moment in preparation of finely disperse materials is the use of different compacting methods, which increases the rate of solid-phase reactions. The active occurrence of glass formation reactions in the temperature region below 950°C allows organizing synthesis of glass granulate without using refractories.

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[2] Here and below: mass content.

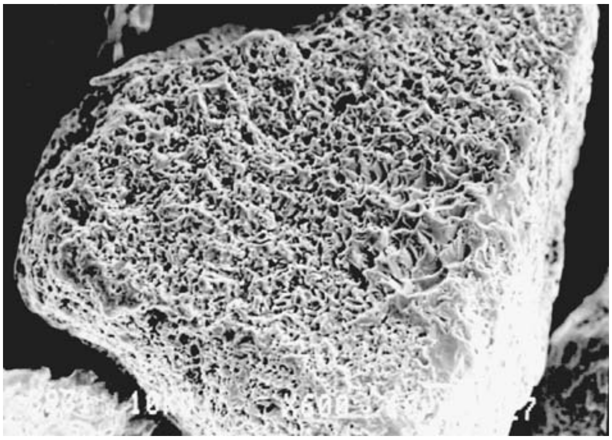

Fig. 1. Electron microscopic photograph of Tuganskoe sand.

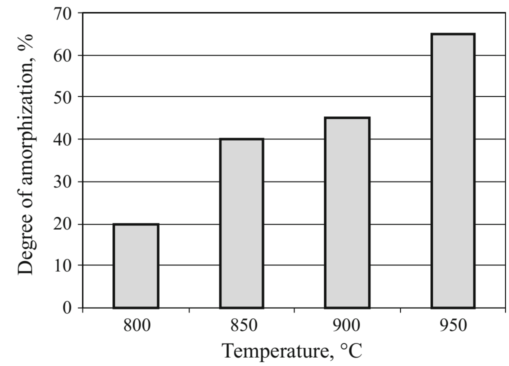

Fig. 2. Degree of x-ray amorphization of samples as a function of thermal treatment of the batch.

The generally accepted foam-glass production technologies are based on existing sheet and bottle glass compositions, so that a three-component composition (%) was initially selected for production of glass granulate: 73 SiO_2, 13 RO, 14 Na_2O. In the phase diagram of the $Na_2O - CaO - SiO_2$ system, this composition is in the region of minimum crystallization, the best chemical stability, and corresponds to industrial bottle glass compositions. The basic components of the initial batch are high-silica material (glass former), the basic component (fluxing agent), and alkaline-earth materials that primarily affect the viscosity properties of the melt.

Reducing the amount of residual crystalline phase to the minimum is a necessary condition for production of quality glass granulate; as an analysis of the glass formation process shows, it is present in the case of low-temperature synthesis. The positive effect of the method of mechanical activation of a substance by absorption of external elastic energy by the substance on the completeness of silicate- and glass-formation reactions is well known. The essence of the method consists of creating a layer of a disordered substance with a different degree of activity on the surface of the particles. A mechanically activated mixture of quartz sand and low-melting soda was previously fabricated by low-temperature synthesis to obtain quality glass granulate and modify the residual crystalline phase. Combined grinding of the constituents of the batch allows attaining not only uniform mixing but also mechanical incorporation of one substance in the surface layers of the other. The mixture obtained can be considered a precursor — the initial component and participant in intermediate reactions of synthesis of the glass phase.

The findings of thermogravimetric analysis showed that batches based on jointly activated quartz sand and soda have the highest chemical activity in the silicate formation stage. The weight losses in heat treatment of this batch due to liberation of CO_2 are approximately 3 times higher than for a batch of the same composition in the same activated sand. For batches with a different ratio of sand and soda, the maximum weight losses were observed in the batches having the higher silicate ratio.

A granulated batch based on a previously mechanically activated mixture of Tuganskoe sand with soda followed by incorporation of the other components of the batch — fluxing agents, where the amount of glass phase obtained is a function of the ratio of the other components, was used to prepare the glass granulate.

The cake of basic silicates with silica formed as a result of silicate formation reactions undergoes physicochemical changes related to an increase in the amount of melt in the system and dissolution of residual silica in the melt in holding for 20 min in the 800 – 950°C range.

According to the data from x-ray phase analysis, the cake is represented by a glassy phase and an insignificant amount of residual silica whose crystal size does not exceed 10 μm (optical analysis). It was found that the amount of glass phase, determined with a specially developed method (measurement of the amount of glass according to GOST 9758–86), was within 90 – 95% and was a function of both the chemical composition of the batch and the heat treatment conditions. The glass phase content increased with an increase in holding at the maximum temperature.

The data from x-ray phase analysis were used to quantitatively assess the unreacted quartz. The relative degree of x-ray amorphization (glass formation D_{gl}) in the heat-treated cakes;

$$D_{gl} = (I/I_0) \times 100,$$

where I and I_0 are the absolute intensity of the amorphous halo for the sample and the initial cullet, respectively.

The histogram of the relative degree of x-ray amorphization of the samples as a function of the batch treatment temperature (Fig. 2) shows that the glass formation process takes place most actively when the temperature is increased to 950°C, and the degree of amorphization increases by 3 times and is 65%.

As a result of grinding the glass granulate to a minimum specific surface area of 5000 cm^2/g and mixing with a blow-

TABLE 1

Material*	Density, kg/m^3	Compressive strength in cylinder, MPa	Thermal conduction, W/(m · K)
Granulated foam glass from cullet	200	1.0	0.08
Granulated foam-glass crystalline material from glass granulate	180 – 250	1.0 – 2.5	0.08 – 0.09

* Water absorption was 4 – 5%.

ing agent, a foamy mixture was obtained and rolled in a plate granulator to prepare the granulated material. Foaming of the granulated mixture in an electric conveyor tunnel furnace at 850°C allowed obtaining a foam-glass crystalline material of different density. As a function of the type of blowing agent, the density of the materials varied from 180 to 250 kg/m^3. A comparative characterization of the properties of foam glass and the foam-glass crystalline material is shown in Table 1.

Compositions and a method for production of foam-glass crystalline materials from natural finely disperse silica-containing raw material by low-temperature synthesis without conducting all stages of the glass-melting process were thus developed based on the new process solutions. We are currently conducting studies on developing the formula and process parameters for production of foam-glass crystalline materials from such natural materials as zeolite, marshalite, diatomite, flask, tripolite, and technogenic wastes, and heat and electric power plant ash and slag, possible versions of preparation of the mixture are being examined, and process schemes are being developed.